Study of Crystal Structure, Strain Tensor, Raman Spectra and Magnetic Properties of V_6O_{13} at Low Temperature

A

Project Report

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To

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CERTIFICATE

This is to certify that the project titled "**Study of Crystal Structure, Strain Tensor, Raman Spectra and Magnetic Properties of V_6O_{13} at Low Temperature**" has been successfully completed by **Ridham Mahajan, Suraj Chauhan, Mohit Sharma, Mohd Shakeel**, **Mandeep Kumar** and **Harsh Dev**, students of the 5th semester, Department of Physics, Cluster University of Jammu, under the supervision of Dr. Dinesh Jasrotia, Department of Physics, Cluster University of Jammu. The project demonstrates the students' ability to conduct independent research, analyse data, and draw meaningful conclusions. Their work is original and well-presented, and they have shown a deep understanding of the subject matter.

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Declaration

We, the undersigned students of the 5th semester, hereby declare that the project titled **Study of Crystal Structure, Strain Tensor, Raman Spectra and Magnetic Properties of V_6O_{13} at Low Temperature** " is our own original work, carried out under the supervision of **Dr. Dinesh Jasrotia**, Professor, Department of Physics, Cluster University of Jammu. The project has not been submitted elsewhere for any examination. We have adhered to the ethical guidelines for research and have not engaged in any plagiarism.

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Acknowledgement

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ABSTRACT

Vanadium oxide (V_6O_{13}) is a promising cathode material for future batteries due to its high theoretical capacity, good cycling stability, and environmental friendliness. In this study, we investigated the crystal structure, vibrational behaviour, morphic effect, and magnetic properties of V_6O_{13} at Low temperature. We determined that V_6O_{13} has a point group of Cs(m) and a space group of Pc at low temperature. The Wyckoff position of V_6O_{13} is 2a, and the lattice distortion between V_2O_5 and V_6O_{13} is 1.72156. V_6O_{13} exhibits a complex and distorted crystal lattice with a morphic effect that can be reversibly altered by applying an electric field. The magnetic space group for V_6O_{13} is Pc (7.24) and its magnetic point group are 1 & m. V_6O_{13} exhibits a combination of ferromagnetic and antiferromagnetic interactions, which creates a favourable electronic environment for lithium-ion intercalation and enhances the battery's capacity and rate capability.

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Chapter 1

Introduction to Solid State Physics

Solid-state physics is a branch of physics that studies rigid matter. It's the largest branch of condensed matter physics.

1.1 Matter:

Matter is everything around us that has mass and takes up space. It's what makes up the physical world. Matter can exist in different forms, which we call the "states of matter." In simple language, here are the main states of matter.

Types of Matter

- Solid: Solids are things that are hard and have a fixed shape. Think of a book or a toy. The particles (tiny pieces) in a solid are packed tightly together, so they can't move around much. That's why solids keep their shape.
- Liquid: Liquids are things that can flow and take the shape of their container. Water is a good example. The particles in a liquid are still close together, but they can move past each other, which is why liquids can flow.
- Gas: Gases are things that can spread out and fill a space. The air we breathe is a gas. In gases, the particles are very far apart and move around freely. That's why gases don't have a fixed shape.

So, matter can be a solid, a liquid, or a gas depending on how closely the particles are packed and how they move. You can think of matter as the "stuff" that makes up everything you see and touch in the world! Solids are one of the four fundamental states of matter, along with liquid, gas, and plasma. Solids are characterized by:

- ✓ Closely packed molecules with the least amount of kinetic energy
- ✓ Structural rigidity and resistance to force applied to the surface
- ✓ Fixed shape and volume
- ✓ Difficulty to compress
- ✓ Particles that can only vibrate about their mean position and cannot move

1.2 Types of Solids

Crystalline Solids:

Crystalline solids have the following properties:

- A three-dimensional geometrical structure.
- A regular, repeating arrangement of atoms, ion, or molecules.
- A sharp melting points.
- A strong, ordered structure.
- Non-conductivity of electricity.
- Anisotropic Nature, meaning they have different properties in different directions
- Structural units (atoms, ions, etc) that only have vibrational motion about their mean position.

Amorphous Solids:

- They don't have a long-range, regular atomic order.
- They form irregular shapes.
- They soften over a range of temperatures depending on their composition and thermal history.
- They fracture in irregular, unpredictable patterns.
- They don't have a sharp melting point.
- Their physical properties are the same in all directions.

These solids lack an ordered internal structure. Examples include glass, rubber, and plastics.

1.3 Lattice

A lattice in solid state is a three-dimensional arrangement of atoms, molecules, or ions in a crystalline solid. It's also called a crystal lattice or space lattice. While drawing lattice structure of a crystal atoms, molecules or ions are represented by point. [1]

Basis

Basis is an atom or group of atoms represented by a single point by attaching the basis to each lattice point we will get crystal structure it is also called Motif.

Lattice + Basis (Motif) = Crystal

Unit Cell

It is the smallest unit of Crystal Lattice which on continuous repetitions can generate whole lattice. This is the representative of crystal structure.

Types of Unit Cell

- Primitive: Lattice point belong only to the corners of the unit cell.
- Non – Primitive: Lattice points belongs to the corners as well as some other positions of the unit cell.

1.4 Bravais Lattices

Table 1.1 Types of Lattices in 2D

Crystal Structure	Bravais Lattice	Conditions	
Square	Square Primitive	$a = b$	$\gamma = 90°$
Rectangular	Rectangular Primitive	$a \neq b$	$\gamma = 90°$
	Rectangular Centred		
Hexagonal	Hexagonal Primitive	$a = b$	$\gamma = 120°$
Oblique	Oblique Primitive	$a \neq b$	$\gamma \neq 90°$

Table 1.2 Types of Lattices in 3D

Crystal Structure	Bravais Lattice	Conditions	
Cubic	Simple	$a = b = c$	$\alpha = \beta = \gamma = 90°$
	Body Centred		
	Face Centred		
Trigonal	Simple	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
	Body Centred		
Orthogonal	Simple	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
	Body Centred		
	Face Centred		
	Base / End Centred		
Trigonal	Simple	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	Simple	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Monocline	Simple	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$
	Base Centred		
Triclinic	Simple	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$

1.5 Miller Indices: ($h\ k\ l$)

Miller indices are a series of numbers that describe the orientation of a plane or set of planes in a crystal lattice. They are defined as the reciprocals of the fractional intercepts that the plane makes with the crystallographic axes

Miller indices are a group of three numbers h, k , and l. They are written in the order a, b, c, except for the Trigonal and Hexagonal Crystal Systems.

Miller Indices are written within small brackets without commas i.e. ($h\,k\,l$)

$$h:k:l = \frac{a}{OA}:\frac{b}{OB}:\frac{c}{OC}$$

Where, a, b, c are the lattice parameters along x, y, z – axis respectively.

OA, OB, OC are the intercepts on x, y, z – axis respectively.

And h , k , l are the Miller Indices.

Inter-Planer Spacing for Cubic crystal

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Table 1.3 Properties of Cubic Crystal

Parameter	Simple Cubic	Face Centred	Body Centred
Volume	a^3		
Density	$\rho = \frac{Mn}{Na^3}$		
No. of Atoms per Unit Cell	1	4	2
Coordination No.	6	12	8
Atomic Radius	$r = \frac{a}{2}$	$r = \frac{a}{2\sqrt{2}}$	$r = \frac{\sqrt{3}}{4}a$
Packing Fraction	0.52	0.74	0.68

1.6 X – RAYS

X-rays are a type of electromagnetic radiation that can pass through most objects, including the body. They are similar to visible light, but have higher energy. X – Ray being Electromagnetic Radiation, also undergo the phenomenon of diffraction as observed for visible light. However, unlike visible light X – Ray cannot be diffracted by ordinary grating because

of their very short wavelength. In 1912, German Physicists Max Van Laue suggested the use of single crystal.

1.6.1 X–Ray Diffraction [2]

When an atomic electron is radiated by a beam of monochromatic X – Rays, it starts vibrating with a frequency as that of X–Rays. Since an accelerating charge emit radiations, the vibrating electron present inside a crystal become sources of secondary radiations having the same frequency as the incident X–Rays. These radiations spread out in all possible directions. The phenomenon may also be regarded as scattering of X – Rays by atomic electron. If the wavelength of incident X – Rays is quite large as compared to the atomic dimensions, then the scattered rays are in phase with each other. However, the scattered radiations are out of phase with each other. So, these radiations undergo constructive and destructive interference with each other at different Positions.

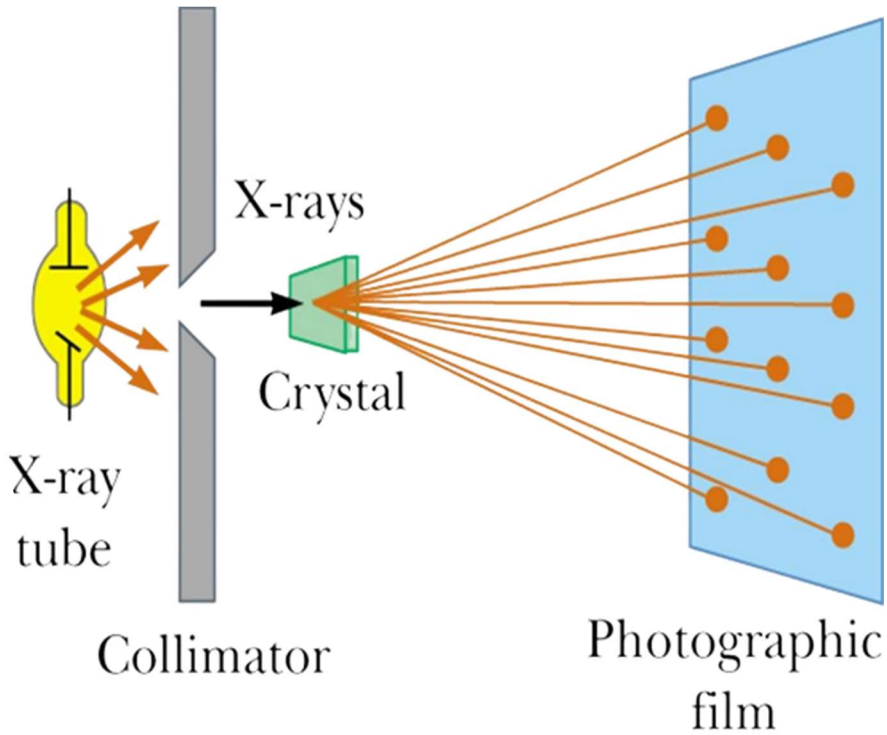

Figure 1.1 X – Ray Diffraction

<u>Condition for X – Ray Diffraction</u>

- Bragg's Law

$$n\lambda = 2\,d\,sin\,\theta$$

The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence (θ, λ).

The variable d indicates the distance between the atomic layers, and the variable The variable d indicates the distance between the atomic layers, and the variable **λ** specifies the wavelength of the incident X-ray beam and n as an integer.

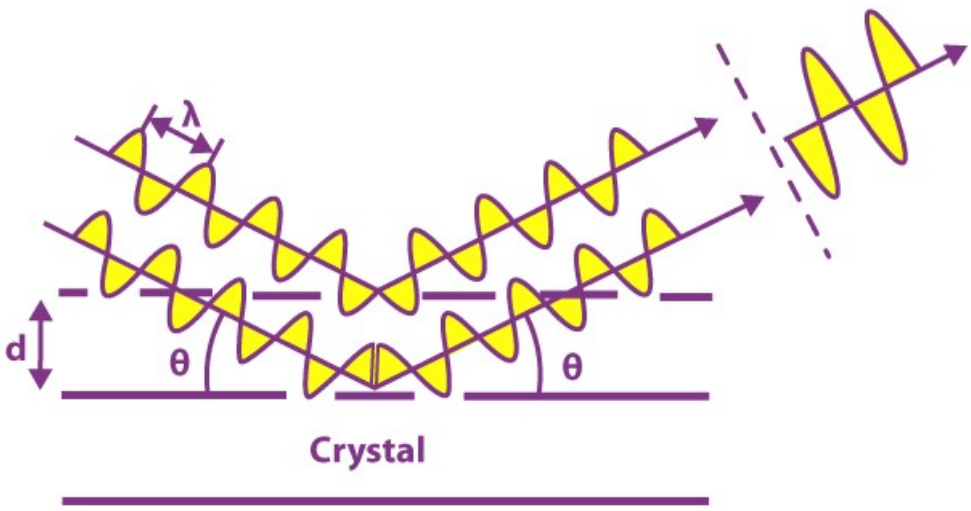

Figure 1.2 Condition for X – Ray Diffraction

This observation illustrates the X-ray wave interface, called X-ray diffraction (XRD) and proof of the atomic structure of crystals.

1.6.2 Applications of X – Ray

X-ray crystallography is a technique that uses X-rays to determine the molecular structure of a crystal. It is based on the principle that X-rays are diffracted by the atoms in the crystal, and the resulting diffraction patterns can be used to reconstruct the 3D structure of the crystal.

X-ray crystallography has many applications in various fields of science, such as:

- **Proteomics**: X-ray crystallography can reveal the 3D structure of proteins, which are essential for understanding their function, interaction, and regulation in biological systems. For example, X-ray crystallography was used to determine the structure of haemoglobin, insulin, and DNA.
- **Mineralogy**: X-ray crystallography can identify minerals by their characteristic diffraction patterns, which reflect their chemical composition and crystal structure. For example, X-ray crystallography was used to discover new minerals, such as quasicrystals.

- **Materials science**: X-ray crystallography can analyse the properties and behaviour of materials at the atomic level, such as their crystalline integrity, grain orientation, grain size, film thickness, and interface roughness. For example, X-ray crystallography was used to study the structure and properties of alloys, ceramics, polymers, and nanomaterials.

1.6.3 History of X-Ray in crystallography

X-ray crystallography has a rich history and has been instrumental in the development of many scientific fields. Here are some key historical points:

1. **Discovery of X-rays**: German engineer Wilhelm Rontgen discovered X-rays in 1895. The photon concept was introduced by Albert Einstein in 1905 and was accepted in the 1920s, when it was confirmed by X-ray scattering from electrons.
2. **First Use**: In 1912, German physicist Max von Laue used X-rays to bounce between a crystal's atoms. This marked the beginning of the use of X-ray crystallography.
3. **Development of Technique**: The technique developed by von Laue and the Braggs at the beginning of the twentieth century provided data which, when processed, enabled scientists to calculate the structures of molecules and appreciate their three-dimensional structures.
4. **Advancements**: In its early days, X-ray crystallography determined the size of atoms, the lengths and types of chemical bonds, and the atomic-scale differences among various materials, especially minerals and alloys. It also revealed the structure and function of many biological molecules, including vitamins, drugs, proteins, and nucleic acids such as DNA.
5. **Modern Day**: Now over 100 years old, X-ray crystallography is still the primary method for characterizing the atomic structure of new materials. To date, about 100,000 protein structures have been published in the Protein Data Bank, with almost 10,000 added every year.

This technique has shaped our understanding of the molecular world and continues to be a vital tool in various scientific fields.

Chapter 2

Introduction to Vanadium Oxide (V_6O_{13})

2.1 Vanadium

Vanadium (V) is a chemical element with atomic number 23. It is a hard, silvery-grey, malleable transition metal. Vanadium was discovered in 1801 by Andrés Manuel del Rio. It got its name "vanadium" in 1831 from the Norse Goddess Vanadis, meaning beauty and fertility.

Vanadium is rarely found in its pure metal form in nature because it easily reacts with oxygen, nitrogen, and even carbon at high temperatures. It is more commonly found in minerals such as vanadinite, carnotite, and patronite.

Vanadium is essential in specific steel alloys, providing extra strength and protection against rust and corrosion. It is also used in catalysts, batteries, and other industrial applications. Vanadium is an essential trace mineral for humans and other animals. It is involved in several important biological processes, including the metabolism of carbohydrates and fats, the regulation of blood sugar levels, and the formation of bones and teeth.

Vanadium Oxides

Vanadium is a transition metal with a complex electronic configuration. Its ground state electronic configuration is $[Ar]3d^3 4S^2$. However, vanadium can also exist in a variety of oxidation states, ranging from 0 to +5. This is because vanadium has five valence electrons in its 3d and 4s orbitals.

The different oxidation states of vanadium give rise to a variety of different vanadium oxides. For example, vanadium(II) oxide (VO) is formed when vanadium loses two of its valence electrons. Vanadium(III) oxide (V_2O_3) is formed when vanadium loses three of its valence electrons, and so on.

Some of the most common vanadium oxides include:

- Vanadium(II) oxide (vanadium monoxide), VO
- Vanadium(III) oxide (vanadium trioxide), V_2O_3
- Vanadium(IV) oxide (vanadium dioxide), VO_2
- Vanadium(V) oxide (vanadium pentoxide), V_2O_5

In addition to these principal oxides of vanadium, various other distinct phases exist:

- Phases with the general formula V_nO_{2n+1} exist between V_2O_5 and VO_2. Examples of these phases include V_3O_7, V_4O_9 and V_6O_{13}.
- Phases with the general formula V_nO_{2n-1} exist between VO_2 and V_2O_3 Called Magnéli phases. Examples of Magnéli phases include V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13} and V_8O_{15} [3].

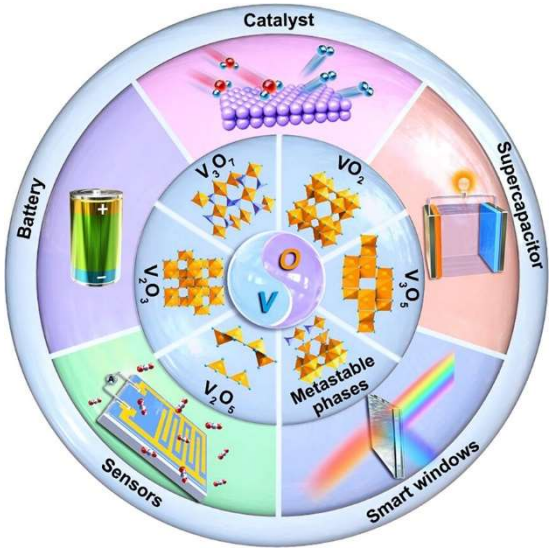

Figure 2.1 Schematic illustration of the thermodynamically stable vanadium oxides and their applications.

Each of these vanadium oxides has its own unique properties and applications. For example, vanadium(V) oxide (V_2O_5) is a yellow-brown solid that is used as a catalyst in a variety of industrial reactions. Vanadium(IV) oxide (VO_2) is a blue-black solid that is known for its dramatic phase transition at around 68 °C. This phase transition can be used to create smart windows that can change from transparent to opaque in response to temperature.

2.2 V_6O_{13}

Vanadium oxide V_6O_{13} is a promising material for use in lithium-ion batteries, sodium-ion batteries, magnesium-ion batteries, zinc-ion batteries, and other types of batteries. It is a mixed-valence compound, meaning that it contains two different oxidation states of vanadium, V^{4+} and V^{5+}. This gives V_6O_{13} a unique structure and properties that make it well-suited for battery applications. It is a black solid that is insoluble in water and most acids. V_6O_{13} has a complex crystal structure that is still not fully understood.

The SEM images of the pristine V_6O_{13} samples are shown in Fig. 2.2 Sample of V_6O_{13} has a 3D flowerlike structure [4].

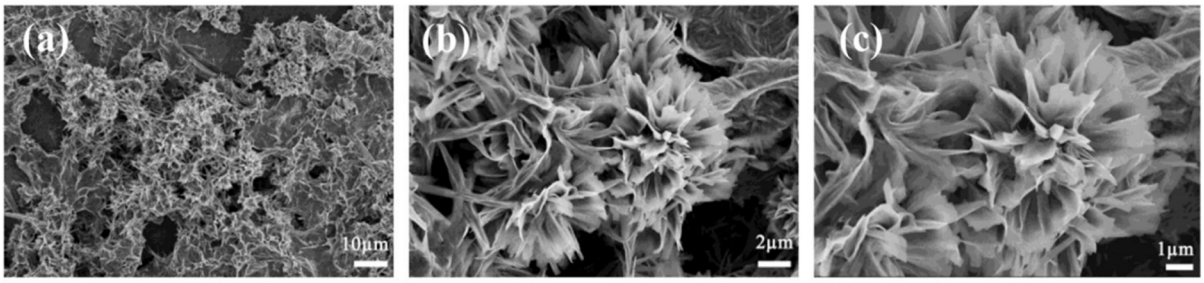

Figure 2.2 SEM image of V_6O_{13} Sample.

2.3 Properties of V_6O_{13}

V_6O_{13} is a relatively rare compound, but it has a number of interesting properties and potential applications. Here are some of the main properties of V_6O_{13}.

1. One of the most notable properties of V_6O_{13} is its high electrical conductivity. This makes it a promising material for use in batteries, fuel cells, and other energy storage devices.
2. V_6O_{13} exhibits a metallic character at room temperature, which is beneficial for high-rate charge and discharge. When it is used as a lithium ion battery electrode material, 8 mol Li^+ intercalated per formula unit endowing a high theoretical specific capacity of 417 mAh g^{-1} and energy density of 900 Wh kg^{-1}[5].
3. V_6O_{13} is also a good catalyst for a variety of reactions, including the oxidation of hydrocarbons and the production of hydrogen. V_6O_{13} is a good catalyst because it can form alkyl oxide with aliphatic alcohol, which can be excited by visible light to

effectively activate the C-H bond of α-C. The catalyst can effectively activate toluene C(sp^3)-H bond into benzyl with the activation energy of 14.2 kcal mol^{-1} [6]

4. V_6O_{13} undergoes a metal-insulator transition at 150K, accompanied by a structural distortion and charge redistribution. The V(1) ions become more V^{5+} like while the V(2) and V(3) ions become more V^{4+} like [7].
5. V_6O_{13} single crystals exhibit both metallic reflection (only above T≃150K) and discrete resonances (four at E || B and three at E ⊥ B) in both semiconductor and metallic phases [8].
6. V_6O_{13} exhibits good electrochemical performance, including high capacity, rate capability, and cycle stability. This means that V_6O_{13} batteries can deliver a high amount of energy, charge and discharge quickly, and last for many cycles.
7. In addition to its electrical and catalytic properties, V_6O_{13} also has a number of other interesting properties, such as its ability to undergo reversible phase changes and its strong magnetic properties.
8. Vanadium has a magnetic moment of 1.73 BM in the free state. When vanadium is oxidized to V_6O_{13}, its magnetic moment increases to approximately 4 BM. This is because the crystal structure of V_6O_{13} forces the vanadium atoms to align their magnetic moments in the same direction.

2.4 Application of V_6O_{13}

These properties are still being investigated, but they could lead to new and innovative applications for V_6O_{13} in the future. Here are some specific examples of the potential applications of V_6O_{13} :-

- **Li-ion Batteries**: V_6O_{13} is a promising material for use in batteries, such as lithium-ion batteries. Vanadium oxide (V_6O_{13}) stands out as a promising cathode material for lithium-ion batteries. The battery developed using V_6O_{13} demonstrates a high specific capacity of 233 mAh g^{-1} at 100 mA g^{-1} of specific current and maintains 91% capacity after 500 cycles [9]

- **Other types of batteries**: V_6O_{13} is also being investigated as a cathode material for other types of batteries, such as magnesium-ion batteries and zinc-ion batteries. These batteries have the potential to be more energy-dense and safer than lithium-ion batteries.

- **Fuel cells**: Vanadium oxide (V_6O_{13}) can be used in fuel cells to extend the power output even when the fuel supply is interrupted. This is because V_6O_{13} can store charge and release it slowly over time. The charge storage mechanism in V_6O_{13} based fuel cells is complex and involves multiple factors, including the oxidation of the V_6O_{13} anode This could be useful for ultra-miniaturization of power sources for mobile energy [10].
- **Environmental remediation**: V_6O_{13} can be used as a catalyst for the oxidation of hydrocarbons. This could be used to clean up oil spills and other environmental contamination.
- **Super-capacitors**: V_6O_{13} can also be used as an electrode material for super-capacitors. Super-capacitors are energy storage devices that can store and release energy much faster than batteries. V_6O_{13} is a promising electrode material for super-capacitors due to its high theoretical capacity, good rate capability, and long cycle life. Tungsten doping can further improve the electrochemical performance of V_6O_{13} nanostructures for super-capacitor applications. In short, V_6O_{13} is a promising electrode material for super-capacitors [11].
- **Gas sensors**: V_6O_{13} can also be used as a gas sensor material. Gas sensors are devices that can detect the presence of specific gases. V_6O_{13} is useful for gas sensor because it has high selectivity in adsorption to H_2S gas with 132 % response magnitude at 350 °C and 60 ppm. The response and recovery times are 32 and 129 s respectively which is remarkably short compared with the data in literatures. This V_6O_{13} sensor was ranked with its V_2O_5 counterpart and still found to be 238.5 % higher for H_2S gas [12].

V_6O_{13} is a fascinating and versatile material with a wide range of potential applications. As research continues, it is likely that we will find even more ways to use V_6O_{13} to improve our lives.

2.5 Crystal Structure of V_6O_{13}

Vanadium oxide (V_6O_{13}) has a complex crystal structure that is characterized by alternating single and double vanadium oxide layers (VO_6 octahedra). The VO6 octahedra are connected to each other by corner-sharing oxygen atoms, which form a tunnel-like structure as shown in figure 2.3. This tunnel-like structure allows for fast and efficient diffusion of lithium ions, which is important for high-rate charge and discharge in batteries.

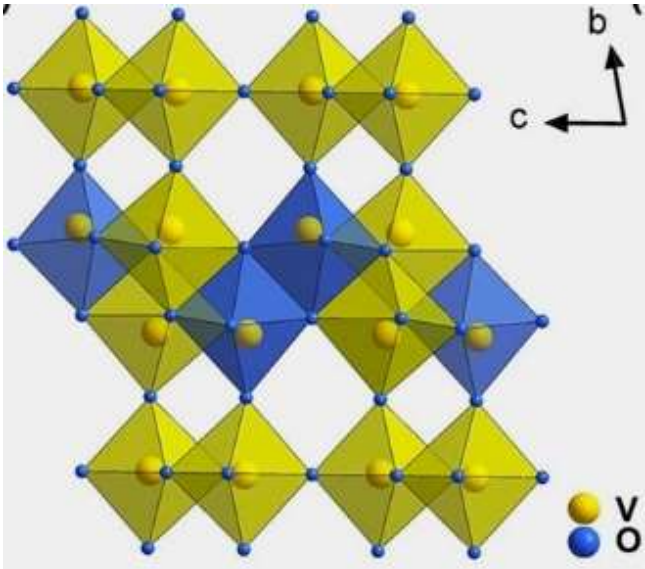

Figure 2.3 Crystal structure of V_6O_{13} with V two types of VO_6 octahedra [13]

Table 2.2 crystallographic details of V_6O_{13}

Lattice Structure	Monoclinic
Space Number	7
Space Group (low Temp.)	Pc
Space Group (Room Temp.)	C2/m
Point Group	C_S (m)
Lattice Parameters	a=10.060 Å, b=3.710 Å, c=11.9633 Å α=90°, β =100.927°, γ =90°
Volume	438.52 $Å^3$

2.6 XRD of Vanadium Oxide

Vanadium oxide (V_6O_{13}) has a layered crystal structure, with the vanadium atoms arranged in octahedral sheets. The X-ray diffraction (XRD) pattern of V_6O_{13} is characterized by a number of peaks at 2θ values of 25.5°, 26.5°, and 30.5°, corresponding to the (110), (003), and (-401) planes respectively. The strong peak at 2θ = 25.5° corresponds to the (110) plane, which is the basal plane of the layered structure. This indicates that the V_6O_{13} crystals are oriented with their basal planes parallel to the sample surface. The medium peak at 2θ = 26.5° corresponds to the (003) plane, which is perpendicular to the basal plane. The weak peaks at 2θ = 30.5° correspond to the (-401) plane respectively [14].

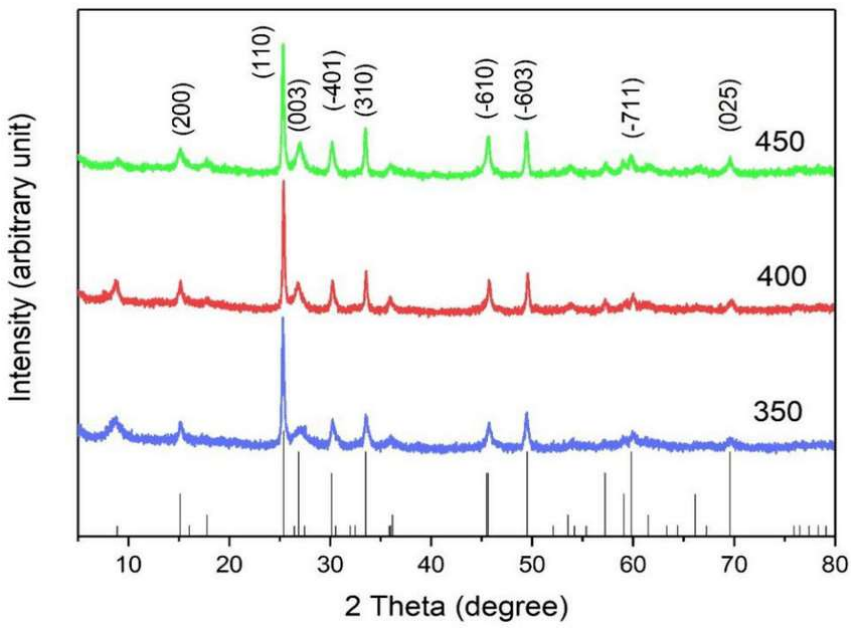

Figure 2.4 The XRD patterns of Vanadium Oxide (V_6O_{13})

The width of the XRD peaks is relatively narrow, indicating that the V_6O_{13} crystals are relatively large. The XRD pattern also shows only the peaks expected for V_6O_{13}, indicating that the material is phase pure. Overall the XRD pattern of V_6O_{13} is consistent with a layered structure with relatively large and phase-pure crystals. This structure is responsible for many of the unique properties of V_6O_{13}, such as its high electrical conductivity and its ability to intercalate lithium ions.

V_6O_{13} is a promising material for a variety of applications, including lithium-ion batteries, electrochromic devices, and gas sensors. The unique structural properties of V_6O_{13}, as revealed by XRD, play a key role in its performance in these applications.

Chapter 3

Space Group Symmetry

3.1 Introduction

Symmetry operations in solid state physics play a fundamental role in understanding the properties and behaviour of crystalline materials. These operations involve transformations that leave a crystal's structure unchanged, helping to classify and describe its symmetrical features. By analysing symmetry, scientists can predict various physical phenomena, such as electronic band structures, optical properties, and vibrational modes, making it a crucial concept for elucidating the unique characteristics of crystalline solids. Symmetry operations include translations, rotations, reflections, and inversions, and their study provides insights into the symmetrical aspects of crystalline lattices and their impact on material properties.

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3.1.1 Symmetry operations

Symmetry operations in solid-state physics are specific transformations that can be applied to a crystal lattice without changing its overall structure. These operations are crucial for understanding and characterizing the symmetrical properties of crystalline materials. Common symmetry operations include:

Translation: Moving the crystal by a fixed distance along one of its lattice vectors, which preserves the lattice structure.

1. Rotation: Rotating the crystal around a specific axis by a certain angle while maintaining its periodic arrangement.
2. Reflection: Mirroring the crystal across a plane, which leaves the crystal's internal arrangement unchanged.

3. Inversion: Reversing the positions of all atoms in the crystal about a central point, often called the inversion centre.
    - Glide and Screw Symmetry: These operations combine translation and rotation to create more complex symmetrical elements within the crystal lattice.

The study of symmetry operations helps researchers classify crystals into different point groups, understand their properties, and predict various physical phenomena. Symmetry considerations are essential for analysing electronic band structures, optical properties, and vibrational modes in crystalline solids.

3.2 Point & Space Group

Vanadium oxide V_6O_{13}, a layered material with promising electrochemical properties, exhibits a unique crystal structure that can be described by its point and space group.

- Point Group

The point group of a material describes its symmetry under rotations about a single point. For V_6O_{13}, the point group is Cs (m). This indicates that the crystal structure of V_6O_{13} has a mirror plane (m) and a two-fold rotational axis (2) passing through the center of the unit cell.

- Space Group

The space group of a material describes its symmetry under translations and rotations in three-dimensional space. For V_6O_{13}, the space group is P_C[15]. This indicates that the crystal structure of V_6O_{13} has a primitive lattice (P), a two-fold screw axis (2), and a glide plane (c).

3.3 Wyckoff Position of space group

In the context of crystallography and solid-state physics, the Wyckoff position refers to the specific positions within a unit cell of a crystal where atoms or ions can be located while maintaining the symmetry of the crystal lattice. Each Wyckoff position is associated with a letter or a symbol, and it represents an equivalent set of positions that can be occupied by the same type of atom or ion. These positions are often described in terms of fractional coordinates relative to the unit cell's parameters.

Wyckoff positions are essential for characterizing the arrangement of atoms or ions in a crystal structure and for understanding the symmetry properties of the crystal. They are particularly useful when working with space groups, which describe the symmetry operations and

arrangements within a crystal lattice. The Wyckoff positions help researchers analyse the distribution of atoms within the unit cell and predict various physical properties of the material.

Table 3.1 Wyckoff positions of V_6O_{13}

Material	Wyckoff Position
V1a	2a
V1b	2a
V2a	2a
V2b	2a
V3a	2a
V3b	2a
O1a	2a
O2a	2a
O3a	2a
O4a	2a
O5a	2a
O6a	2a
O7a	2a
O1b	2a
O2b	2a
O3b	2a
O5b	2a
O6b	2a
O7b	2a

The Wyckoff position 2a for V_6O_{13} indicates that the vanadium and oxygen atoms within the crystal lattice are arranged in a specific pattern that is characterized by a two-fold rotational symmetry axis. This arrangement has implications for the material's physical properties, such as its electrical conductivity, optical properties, and vibrational modes.

3.4 Brillouin Zone of Space Group

The Brillouin zone is a concept in solid-state physics used to describe the allowed energy states of electrons in a crystal lattice. The Brillouin zone is a representation of the first Brillouin zone, which is a Wigner-Seitz cell in reciprocal space that corresponds to the symmetry of the crystal lattice. It is also known as the first zone of the reciprocal lattice.

The Brillouin zone is crucial for understanding electronic band structures in crystalline materials. The allowed electronic energy levels are determined by the Brillouin zone's shape and size. For each crystal and its associated space group, the Brillouin zone has a unique geometry and symmetry.

In summary, the Brillouin zone is a fundamental concept in solid-state physics, and its specific shape and size are related to the crystal's space group and lattice parameters. It plays a central role in the study of electronic properties in crystalline solids. The Brillouin zone of V_6O_{13} is shown below [17]:

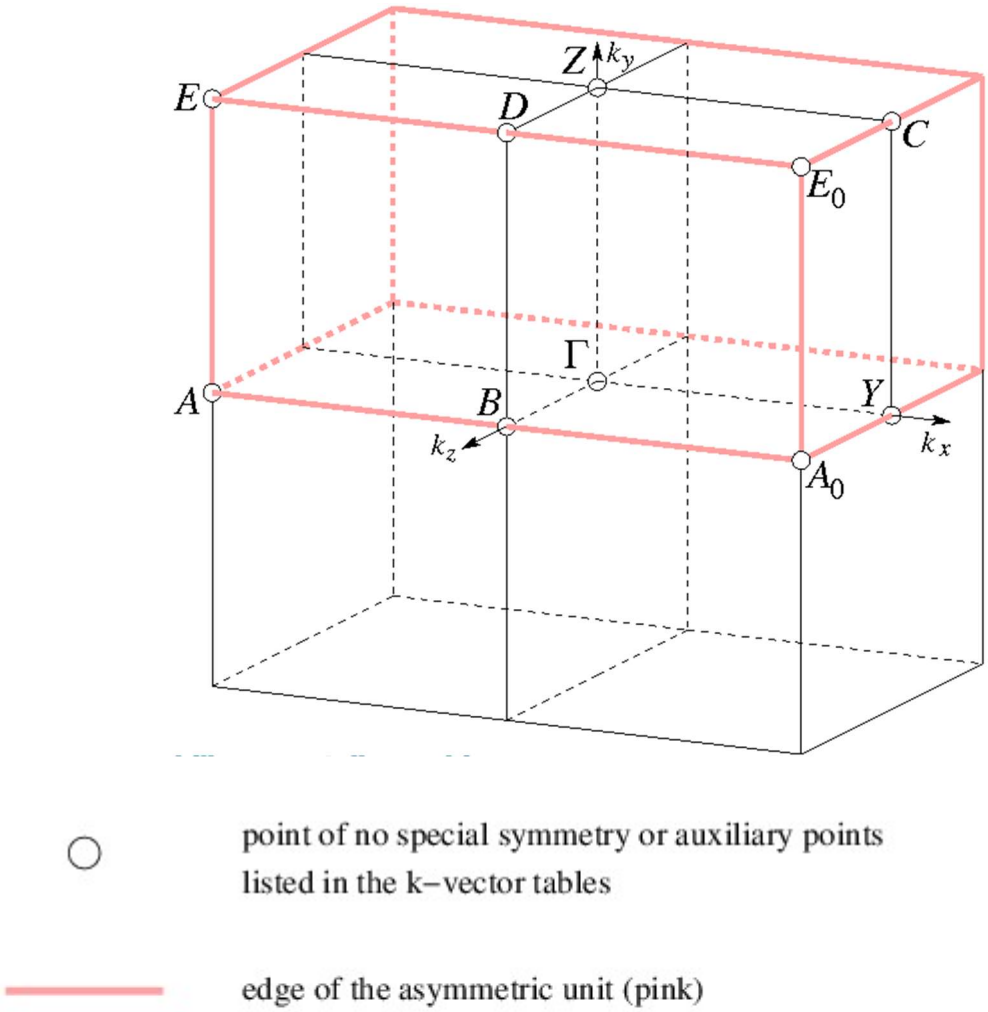

Figure 3.1 Brillouin Zone of V_6O_{13}

3.5 K- vector of space group

In solid-state physics and condensed matter physics, a K-vector (also written as k-vector or simply k) represents a wave vector in the context of periodic structures like crystals. K-vectors are used to describe the electronic band structure and electronic properties of materials.

Specifically, K-vectors are associated with the Brillouin zone, which is the first Brillouin zone of the reciprocal lattice. Each K-vector corresponds to a particular point or wave vector in reciprocal space within the Brillouin zone. The Brillouin zone is determined by the crystal's lattice and its associated space group.

K-vectors play a crucial role in understanding the behaviour of electrons in a crystal lattice. The electronic band structure, energy dispersion, and electronic properties are analysed by considering how electrons move through reciprocal space, with K-vectors representing different allowed states and energy levels for electrons in the material.

The specific K-vectors and their properties depend on the crystal's symmetry, space group, and lattice parameters, making them an essential concept for understanding the electronic properties of crystalline materials.

Table 3.2 K-vector label of V_6O_{13}

Material	K-Vector Label	ITA Classification
V1a	GP	2c
V1b	GP	2c
V2a	GP	2c
V2b	GP	2c
V3a	GP	2c
V3b	GP	2c
O1a	GP	2c
O2a	GP	2c
O3a	GP	2c
O4a	GP	2c
O5a	GP	2c
O6a	GP	2c
O7a	GP	2c
O1b	GP	2c
O2b	GP	2c
O3b	GP	2c
O5b	GP	2c
O6b	GP	2c
O7b	GP	2c

Chapter 4
Structure utility

4.1 Strain Tensor

The Strain program is used to calculate the linear and finite strain tensor for two given unit cells. The strain tensor is a measure of how much a material has deformed and can be used to predict the elastic properties of the material. The degree of lattice distortion, which can be measured by the strain tensor, has a significant impact on the elastic properties of crystalline materials.

The strain determination method has been used to compare the unit cell parameters of two materials, V_2O_5 and V_6O_{13}. By constructing their metric tensor and calculating the linear and finite Lagrangian strain tensors, the researchers were able to quantify the degree of lattice distortion in each material. They found that the material with the higher degree of lattice distortion also had higher elastic moduli. This finding suggests that the degree of lattice distortion can be used to predict the elastic behaviour of materials. This information could be used to design new materials with tailored elastic properties for specific applications.

A higher degree of lattice distortion will cause the atoms in the crystal to be closer together in some directions and further apart in other directions. This can lead to changes in the elastic properties of the material. For example, a material with a high degree of lattice distortion may be stiffer in one direction than in another.

The strain determination method can be used to measure the degree of lattice distortion in a material by calculating the strain tensor. The strain tensor is a mathematical object that describes the deformation of a material. The degree of lattice distortion can be determined by looking at the eigenvalues of the strain tensor. The eigenvalues of the strain tensor represent the principal strains, which are the maximum and minimum strains in the material. A material with a high degree of lattice distortion will have large principal strains. The strain determination method is a powerful tool for understanding the relationship between lattice distortion and elastic properties in inorganic-organic hybrid materials. This information can be used to design new materials with tailored elastic properties for specific application.

Table 4.1 Parameters of 2 cells

S. No.	Parameters	V_2O_5	V_6O_{13}
1	**Crystal System**	Orthorhombic	Monoclinic
2	**Space Group**	Pmmn	Pc
3	**a, b, c**	11.51, 4.37, 3.56	10.060, 3.710, 11.9633
4	**α, β, γ**	α = β = γ = 90°	α = γ = 90°, β = 100.927°
5	**Volume**	179.06	438.52
6	**No. of Atom**	7	19

4.1.1 Strain tensor calculation

Lattice parameters of cell number 1(undeformed):

```
11.51 4.37 3.56 90.00 90.00 90.00
```

Lattice parameters of cell number 2(deformed):

```
10.06 3.71 11.96 90.00 100.92 90.00
```

Linear Lagrangian Strain Tensor (small deformation)

The linear Lagrangian strain tensor is a measure of the deformation of a material body. It is calculated as follows:

$S = 0.5\ (e + e^T)$

where:

- e is the Green-Lagrange strain tensor, which is defined as: $e = R_2\ R_1^{-1} - I$
- R_1 and R_2 are the standard root tensors of cell 1 and 2, respectively
- I is the 3x3 identity matrix

```
[ -0.141824  0.000000 -0.082839 ]
[  0.000000 -0.151030 -0.000000 ]
[ -0.082839 -0.000000  2.360478 ]
```

Eigenvalues:

```
-0.15103 -0.14456 2.36322
```

Finite Lagrangian Strain Tensor (finite deformation)

The finite Lagrangian strain tensor, also known as the Green-Lagrangian strain tensor, is a measure of the deformation of a material body that is valid for both small and large deformations. It is calculated as follows:

$S = 0.5\ (e + e^T + e^T e)$

where:

- e is the Green-Lagrange strain tensor, which is defined as: $e = R_2 R_1^{-1} - I$
- R_1 and R_2 are the standard root tensors of cell 1 and 2, respectively
- I is the 3x3 identity matrix.

```
[ -0.118042  0.000000 -0.278379 ]
[  0.000000 -0.139625 -0.000000 ]
[ -0.278379 -0.000000  5.146405 ]
```

Eigenvalues

```
-0.13962 -0.13272 5.16108
```

Degree of lattice distortion

```
1.72156
```

$$\text{Degree of lattice distortion} = \frac{\sqrt{\text{sum of squared eigenvalues of strain tensor}}}{3}$$

The strain tensor can be calculated in different ways, depending on the type of deformation. For example, the linear Lagrangian strain tensor is used for small deformations, while the finite Lagrangian strain tensor is used for both small and large deformations.

The degree of lattice distortion between these two materials is a measure of how much the crystal lattice of V_6O_{13} is distorted compared to the crystal lattice of V_2O_5. A higher degree of lattice distortion indicates a greater difference in the crystal structures of the two materials.

In this case, the degree of lattice distortion between V_2O_5 and V_6O_{13} is 1.72156. This relatively high degree of lattice distortion is due to the difference in the coordination number of vanadium atoms in the two materials.

The degree of lattice distortion can have a significant impact on the physical properties of materials. For example, lattice distortion can affect the electrical conductivity, optical properties, and mechanical properties of a material. In the case of V_6O_{13}, the high degree of lattice distortion is thought to contribute to its high theoretical capacity as a cathode material for batteries.

4.2 Assignment of Wyckoff positions

To assign Wyckoff positions to atoms in a crystal structure, you can use the program WPASSIGN. This program requires the space group ITA number, the cell parameters, and the atom positions as input data. The program will only accept structures described in the standard/default setting of the space group. If the original structure is described with respect to an ITA setting, you can use the program SETSTRU to transform it to the standard setting.

Here is a step-by-step guide to assigning Wyckoff positions to atoms in a crystal structure using WPASSIGN:

Make sure that the crystal structure is described in the standard/default setting of the space group. If it is not, use SETSTRU to transform it.

1. Open WPASSIGN and enter the following information:
2. Space group ITA number
3. Cell parameters (separated with spaces)
4. Atom positions (in the standard/default setting)
5. Click the "Assign Wyckoff positions" button.

WPASSIGN will identify the Wyckoff position of each atom and calculate the corresponding atomic orbit.

Here are the Wyckoff positions of each atom of V_6O_{13}

```
# Space Group ITA number
7
# Lattice parameters (lengths in angstorm and angles in degrees)
10.06 3.71 11.96 90 100.927 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
V     1a   2a    -0.006 0.297 0.3456
```

```
V     1b   2a    -0.003 0.235 0.641
V     2a   2a    0.360 0.250 0.417
V     2b   2a    0.632 0.247 0.590
V     3a   2a    0.363 0.248 0.719
V     3b   2a    0.630 0.251 0.288
O     1a   2a    -0.003 0.256 0.183
O     2a   2a    0.385 0.249 0.885
O     3a   2a    0.406 0.252 0.254
O     4a   2a    -0.003 0.240 0.501
O     5a   2a    0.192 0.252 0.386
O     6a   2a    0.196 0.246 0.681
O     7a   2a    0.403 0.251 0.564
O     1b   2a    -0.004 0.241 0.828
O     2b   2a    0.609 0.251 0.121
O     3b   2a    0.587 0.248 0.752
O     5b   2a    0.799 0.246 0.617
O     6b   2a    0.798 0.254 0.322
O     7b   2a    0.588 0.251 0.441
```

Output :-

Atoms data

Atom Type	Wyckoff Position	SS	Representative	Atomic Orbit
V1a	2a (x, y, z)	1	(0.994000,0.297000,0.345600)	(0.994000,0.297000,0.345600) (0.994000,0.703000,0.845600)
V1b	2a (x, y, z)	1	(0.997000,0.235000,0.641000)	(0.997000,0.235000,0.641000) (0.997000,0.765000,0.141000)
V2a	2a (x, y, z)	1	(0.360000,0.250000,0.417000)	(0.360000,0.250000,0.417000) (0.360000,0.750000,0.917000)
V2b	2a (x, y, z)	1	(0.632000,0.247000,0.590000)	(0.632000,0.247000,0.590000) (0.632000,0.753000,0.090000)
V3a	2a (x, y, z)	1	(0.363000,0.248000,0.719000)	(0.363000,0.248000,0.719000) (0.363000,0.752000,0.219000)

V3b	2a (x, y, z)	1	(0.630000,0.251000,0.288000)	(0.630000,0.251000,0.288000) (0.630000,0.749000,0.788000)
O1a	2a (x, y, z)	1	(0.997000,0.256000,0.183000)	(0.997000,0.256000,0.183000) (0.997000,0.744000,0.683000)
O2a	2a (x, y, z)	1	(0.385000,0.249000,0.885000)	(0.385000,0.249000,0.885000) (0.385000,0.751000,0.385000)
O3a	2a (x, y, z)	1	(0.406000,0.252000,0.254000)	(0.406000,0.252000,0.254000) (0.406000,0.748000,0.754000)
O4a	2a (x, y, z)	1	(0.997000,0.240000,0.501000)	(0.997000,0.240000,0.501000) (0.997000,0.760000,0.001000)
O5a	2a (x, y, z)	1	(0.192000,0.252000,0.386000)	(0.192000,0.252000,0.386000) (0.192000,0.748000,0.886000)
O6a	2a (x, y, z)	1	(0.196000,0.246000,0.681000)	(0.196000,0.246000,0.681000) (0.196000,0.754000,0.181000)
O7a	2a (x, y, z)	1	(0.403000,0.251000,0.564000)	(0.403000,0.251000,0.564000) (0.403000,0.749000,0.064000)
O1b	2a (x, y, z)	1	(0.996000,0.241000,0.828000)	(0.996000,0.241000,0.828000) (0.996000,0.759000,0.328000)
O2b	2a (x, y, z)	1	(0.609000,0.251000,0.121000)	(0.609000,0.251000,0.121000) (0.609000,0.749000,0.621000)
O3b	2a (x, y, z)	1	(0.587000,0.248000,0.752000)	(0.587000,0.248000,0.752000) (0.587000,0.752000,0.252000)
O5b	2a (x, y, z)	1	(0.799000,0.246000,0.617000)	(0.799000,0.246000,0.617000) (0.799000,0.754000,0.117000)
O6b	2a (x, y, z)	1	(0.798000,0.254000,0.322000)	(0.798000,0.254000,0.322000) (0.798000,0.746000,0.822000)
O7b	2a (x, y, z)	1	(0.588000,0.251000,0.441000)	(0.588000,0.251000,0.441000) (0.588000,0.749000,0.941000)

4.3 Visualization Structure Using Jmol

Jmol is a free, open-source Java viewer for 3D molecular structures [18]. It is a powerful tool for students, educators, and researchers in chemistry, biochemistry, and other fields dealing with molecular structure. Jmol can be used to render secondary structures of proteins and nucleic acids, produce animations of chemical reactions and conformational changes, visualize vibrations of small molecules, and make changes to structures interactively.

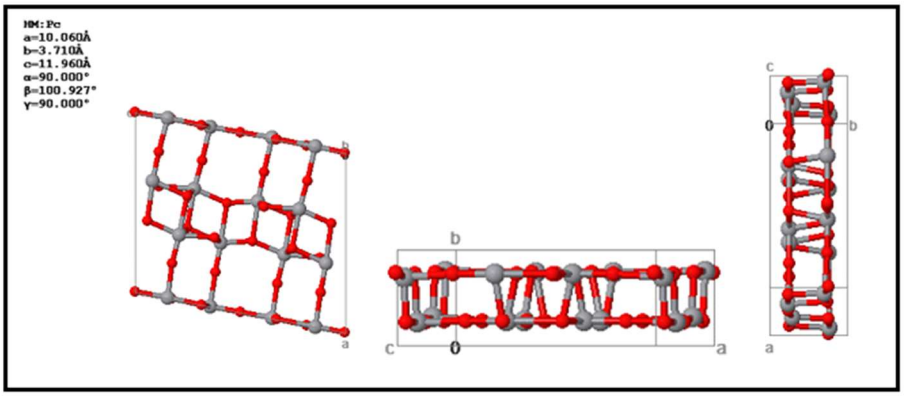

Figure 4.1 3D view of V_6O_{13}

The 3D visualization of vanadium oxide V_6O_{13} reveals a complex and distorted crystal lattice. The vanadium atoms are arranged in a distorted octahedral coordination environment. This distortion is due to the difference in size between the vanadium and oxygen atoms. The vanadium atoms are larger than the oxygen atoms, and they are not able to pack together tightly in a regular arrangement. This distortion has a significant impact on the physical properties of V_6O_{13}, such as its electrical conductivity and optical properties.

The 3D visualization also shows that V_6O_{13} is a layered material. The layers are formed by the V-O chains, and they are held together by weak van der Waals forces. This layered structure is thought to be responsible for the high theoretical capacity of V_6O_{13} as a cathode material for batteries.

Overall, the 3D visualization of V_6O_{13} provides valuable insights into the structure and properties of this material. This information can be used to design new materials with improved properties for a variety of applications.

Chapter 5

Raman & Hyper-Raman Scattering

5.1 Introduction

Spectroscopy is a powerful tool that scientists use to study the chemical composition of matter. It works by sending light at a sample of matter and then measuring how the light interacts with the sample. Different substances interact with light in different ways, so scientists can use spectroscopy to identify and characterize a wide variety of compounds. Raman spectroscopy was named in the honour of its inventor, C.V. Raman. Raman spectroscopy is a branch of vibrational spectroscopy, Raman spectroscopy is a powerful analytical technique that can be used to identify and characterize molecules based on their unique vibrational fingerprints. Raman spectroscopy is based on the inelastic scattering of light. When a photon of light interacts with a molecule, it can be absorbed and re-emitted with a different energy. This energy difference corresponds to the vibrational energy of the molecule. The resulting Raman spectrum is a unique fingerprint of the molecule, and it can be used to identify and characterize unknown compounds.

Raman and hyper-Raman scattering are two types of inelastic scattering of light. In Raman scattering, a photon of light interacts with a molecule and is scattered with a different energy. This energy difference corresponds to the vibrational energy of the molecule. In hyper-Raman scattering, two photons of light interact with a molecule and are scattered with a different energy. This energy difference also corresponds to the vibrational energy of the molecule.

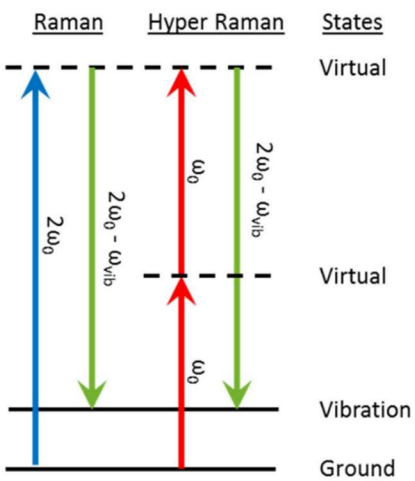

Figure 5.1 Difference between Raman & Hyper- Raman

Raman scattering is a much more common process than hyper-Raman scattering. This is because Raman scattering is a one-photon process, while hyper-Raman scattering is a two-photon process. Two-photon processes are generally much less efficient than one-photon processes. However, hyper-Raman scattering has some advantages over Raman scattering. First, hyper-Raman scattering is more sensitive to certain types of vibrational modes.

5.2 SAM (Spectral Active Modes)

Symmetry-adapted modes (SAM) is a technique that categorizes the normal modes of vibration in a molecular solid based on their symmetry behaviour. It involves identifying the symmetry operations of the system and determining the corresponding irreducible representations, which represent the fundamental vibrational patterns. By constructing linear combinations of normal modes that transform according to each irreducible representation, SAM creates symmetry-adapted modes. These modes exhibit the same symmetry as the corresponding irreducible representation, allowing for a systematic understanding of vibrational properties. SAM is particularly useful for analysing allowed or forbidden vibrational transitions in spectroscopy, as it helps predict which modes are susceptible to infrared (IR) and Raman scattering. The SAM software effectively calculates these modes and their activity in IR and Raman spectra [19].

5.2.1 IR and Raman modes

Infrared (IR) and Raman spectroscopy are two complementary techniques used to study the vibrational modes of molecules and materials. IR spectroscopy measures the absorption of infrared radiation by a sample, while Raman spectroscopy measures the inelastic scattering of light by a sample.

- IR spectroscopy: IR radiation is absorbed by molecules when it causes a change in the dipole moment of the molecule. This means that IR spectroscopy can only be used to study molecules that have a permanent dipole moment.
- Raman spectroscopy: Raman scattering occurs when a photon of light interacts with a molecule and causes a change in its polarizability. This means that Raman spectroscopy can be used to study all molecules, regardless of whether or not they have a permanent dipole moment.

Acoustical and optical modes

The normal modes of vibration in solids can be classified as either acoustical or optical modes.

- Acoustical modes: Acoustical modes are those in which the atoms in the solid move in a coordinated way, like a sound wave. Acoustical modes are always Raman-active, but they are not IR-active unless the solid has a centre of symmetry.
- Optical modes: Optical modes are those in which the atoms in the solid move against each other, like a spring. Optical modes are always IR-active, but they are only Raman-active if the solid does not have a centre of symmetry.

IR Raman and Hyper-Raman Activity for the Space Group *Pc* (No. 7)

Input Structure:

```
7
10.06 3.71 11.96 90 100.927 90
19
V     1a  2a    -0.006000 0.297000 0.345600
V     1b  2a    -0.003000 0.235000 0.641000
V     2a  2a    0.360000 0.250000 0.417000
V     2b  2a    0.632000 0.247000 0.590000
V     3a  2a    0.363000 0.248000 0.719000
V     3b  2a    0.630000 0.251000 0.288000
O     1a  2a    -0.003000 0.256000 0.183000
O     2a  2a    0.385000 0.249000 0.885000
O     3a  2a    0.406000 0.252000 0.254000
O     4a  2a    -0.003000 0.240000 0.501000
O     5a  2a    0.192000 0.252000 0.386000
O     6a  2a    0.196000 0.246000 0.681000
O     7a  2a    0.403000 0.251000 0.564000
O     1b  2a    -0.004000 0.241000 0.828000
O     2b  2a    0.609000 0.251000 0.121000
O     3b  2a    0.587000 0.248000 0.752000
O     5b  2a    0.799000 0.246000 0.617000
O     6b  2a    0.798000 0.254000 0.322000
O     7b  2a    0.588000 0.251000 0.441000
```

The space group it has been introduced is *Pc* (No. 7), its point group is C_s (m)

Mechanical representation

$M = 57A' + 57A''$

More information about the mechanical representation:

Acoustic and Optic modes:

$\Gamma_{acoustic} = 2A' + A''$

$\Gamma_{optic} = 55A' + 56A''$

IR, Raman and Hyper-Raman Active Modes

IR Active Modes

WP	A'	A''
2a	3	3

Infrared active modes: $55A' + 56A''$ (Acoustic modes not included)

Raman Active Modes

WP	A'	A''
2a	3	3

Raman active modes: $55A' + 56A''$ (Acoustic modes not included)

Hyper-Raman Active Modes

WP	A'	A''
2a	3	3

Hyper-Raman active modes: $55A' + 56A''$ (Acoustic modes not included)

IR and Raman Modes for P c (7)

Wyckoff Position: 2a

Mechanical Rep

M = 3A'+3A"

Infrared Active Modes

A', A"

Raman Active Modes

A', A"

Irrep: A'

M	2a	A'	A'	A'
X_1	(x,y,z)	·	1	·
Y_1		·	·	1
Z_1		1	·	·
X_2	(x,-y,z+1/2)	·	1	·
Y_2		·	·	-1
Z_2		1	·	·

Irrep: A"

M	2a	A"	A"	A"
X1	(x,y,z)	·	-1	·
Y1		·	·	1
Z1		-1	·	·
X2	(x,-y,z+1/2)	·	1	·

Y2		·	·	1
Z2		1	·	·

The mechanical representation of acoustic and optic modes in V_6O_{13} provides a framework for understanding the vibrational behaviour of the material at the atomic level. Acoustic modes, associated with the movement of the entire lattice, are responsible for sound propagation, while optic modes, involving relative displacements of atoms within the unit cell, are responsible for infrared and Raman scattering.

5.3 Raman & Hyper-Raman Tensors

Raman and hyper-Raman tensors are mathematical objects that describe how the polarizability of a molecule changes in response to an external electric field. The polarizability of a molecule is a measure of how easily it can be induced to form an electric dipole moment. The Raman and hyper-Raman tensors are important because they allow us to relate the intensity of the Raman and hyper-Raman scattering signals to the vibrational modes of the molecule. This information can be used to identify and characterize the molecule, as well as to study its structure and dynamics.

Raman tensors are second-rank tensors, meaning that they have two indices whereas Hyper-Raman tensors are third-rank tensors, meaning that they have three indices. The Raman & Hyper-Raman tensor for a particular vibrational mode can be calculated using quantum mechanics. Once the tensor is known, the intensity of the Raman scattering signal for that vibrational modes can be calculated.

Raman & Hyper-Raman Tensors for V_6O_{13} are as follows:

Raman Tensors

A'(x,z)			A''(y)		
b	·	d	·	f	·
·	c	·	f	·	e
d	·	a	·	e	·

Hyper-Raman Tensors

A'(x,z)						A''(y)					
b	f	c	·	e	·	·	·	·	k	·	h
·	·	·	g	·	f	h	i	g	·	k	·
e	d	a	·	c	·	·	·	·	g	·	k

5.4 Correlation relation for group-subgroup pairs

In crystallography, a group-subgroup relationship is the relationship between a crystal space group and a subgroup of that space group. A subgroup of a space group is a set of symmetry operations that is contained within the symmetry operations of the parent group. The subgroup may have fewer symmetry operations than the parent group, but it must still contain all of the symmetry operations that are necessary to describe the crystal structure.

Group-subgroup relationships are important in crystallography because they allow us to understand the relationship between different crystal structures. For example, if we know that two crystal structures have the same parent space group, then we know that they are related by a symmetry reduction operation. This means that the two crystal structures have the same basic structure, but one of the crystal structures has fewer symmetry operations due to distortions or other factors.

Group-subgroup relationships can also be used to predict the properties of crystals. For example, the infrared (IR) and Raman spectra of a crystal are related to the symmetry of the crystal's vibrational modes. By studying the group-subgroup relationship between a crystal's space group and the space groups of its subgroups, we can predict which vibrational modes are IR and Raman active. Group-subgroup relationships are a powerful tool for understanding the symmetry and structure of crystals. By studying the group-subgroup relationships between different crystal space groups, we can gain insights into the properties of crystals and how they can be modified.

m	1
A'	A
A''	A

bold IR Active Modes

Raman Active Modes

Hyper-Raman Active Modes

Raman and Hyper-Raman Active Modes

5.5 Morphic Effects

The morphic effect is a change in the physical properties of a material due to the application of an external force. The external force can be an electric field, a magnetic field, or even mechanical stress. The morphic effect is most commonly observed in crystals, but it can also be seen in other materials, such as polymers and metals.

The morphic effect is caused by a change in the symmetry of the material. Symmetry is a measure of how much a material is invariant under certain transformations, such as rotations, reflections, and translations. When an external force is applied to a material, it can break some of the symmetries of the material. This change in symmetry can lead to changes in the physical properties of the material, such as its electrical conductivity, optical properties, and vibrational modes. The morphic effect is a powerful tool that can be used to control the properties of materials.

Morphic Effects for the point group C_s (m)

Input:

- Field: Electric
- Direction: (0,1,0)
- Point group: C_s (m)

Low symmetry group:

- Applying the field in the direction (1,0,0) the symmetry is reduced to the point group C_1 (1)

Transformation matrix: **a, b, c**; 0, 0, 0

Matrix form:

$$P = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

On applying an electric field in the direction (0,1,0) causes a substantial reduction in the material's symmetry from C_s to C_1, indicating a significant structural alteration induced by the

electric field. The transformation matrix for the morphic effect, a, b, c; 0, 0, 0, implies that the electric field primarily affects the a, b, and c lattice parameters, while leaving the remaining lattice parameters unchanged. Moreover, this effect has the potential to change material properties, such as electrical conductivity, optical characteristics, and mechanical properties.

Chapter 6

Determination of Magnetic Behaviour

6.1 Introduction

In the realm of crystallography, the concepts of magnetic space group and magnetic point group play a crucial role in understanding and classifying the magnetic properties of materials. The magnetic space groups can be placed into three categories. First, the 230 colourless groups contain only spatial symmetry, and correspond to the crystallographic space groups. Then there are 230 grey groups, which are invariant under antisymmetric. Finally, are the 1191 black-white groups, which contain the more complex symmetries. Magnetic space groups are represented using a unique international notation system that includes a numerical identifier and a Hermann-Mauguin symbol, providing a comprehensive description of the symmetries present in both the crystal and magnetic structures. Each magnetic space group represent a distinct magnetic arrangement and symmetry which plays a crucial role in understanding the variety of material properties, including ferromagnetism, ferroelectricity.

Magnetic space groups describe the symmetry of a crystal lattice when considering both the arrangement of atoms and the ordering of their magnetic moments. These groups incorporate both spatial and time reversal symmetries, which play crucial roles in understanding the magnetic behaviour of materials.

- Spatial Symmetry:

Spatial symmetry refers to the invariance of a structure under certain geometric transformations, such as rotations, reflections, and translations. Magnetic space groups incorporate these transformations while also considering the orientations of the magnetic moments. This allows for a more comprehensive understanding of the overall symmetry of the magnetic system. For example, a magnetic space group might possess a mirror plane where the magnetic moments on either side of the plane are mirrored images of each other. This information is crucial for predicting the direction and strength of magnetic interactions between atoms within the crystal lattice.

- Time Reversal Symmetry:

Time reversal symmetry implies that a system remains unchanged under the reversal of time. In the context of magnetism, this means the magnetic moments should reverse their direction if time were to rewind. However, most magnetic materials, including V6O13, break this

symmetry. The absence of time reversal symmetry in magnetic space groups leads to unique magnetic properties and behaviours, such as hysteresis and magnetic memory.

6.2 Identification of Magnetic Space Group

The set of generators for V_6O_{13} are:

x,y,z,+1 x,-y,1/2+z,+1

From this set of generators, the magnetic space group has been identified as Pc (No. 7.24). The designation "Pc" in the magnetic space group Pc (7.24) for vanadium oxide (V_6O_{13}) represents a primitive monoclinic crystal lattice with a glide plane along the c-axis. The letter "c" in the magnetic space group Pc (7.24) denotes the presence of a glide plane along the c-axis, which is the z-axis in this case. A glide plane is a symmetry operation that simultaneously reflects the crystal lattice across a plane and translates it by half a lattice vector in the direction of the plane normal. The notation "z+1/2" indicates that the glide plane is located at a distance of half a unit cell along the z-axis.

The combination of primitive monoclinic lattice and a glide plane along the c-axis is characteristic of the Pc magnetic space group. This symmetry group has a significant impact on the magnetic properties of V_6O_{13} contributing to its complex magnetic structure and diverse magnetic behaviour.

6.3 Wyckoff Position of Magnetic Space Group

The Wyckoff positions of a magnetic space group describe the different symmetry-equivalent positions that magnetic atoms can occupy within the unit cell of a crystal structure. These positions take into account both the spatial symmetry of the crystal lattice and the magnetic ordering within the structure. Each Wyckoff position is denoted by a letter, and multiple positions may be associated with the same letter if they are symmetry-equivalent.

Table 6.1 Wyckoff Position and Site Symmetry of Pc

Multiplicity	Wyckoff letter	Coordinates
2	a	(x,y,z | m_x,m_y,m_z) (x,-y,z+1/2 | -m_x,m_y,-m_z)

Site Symmetries of the Wyckoff Positions

WP	Representative	Site symmetry
2a	(x,y,z | m_x,m_y,m_z)	1
2a	(x,-y,z+1/2 | -m_x,m_y,-m_z)	1

The Wyckoff position for vanadium oxide (V_6O_{13}) is found to be 2a. The Wyckoff position of a material can provide important insights into its magnetic properties. In the case of V_6O_{13}, the 2a Wyckoff position helps to explain the complex magnetic structure and diverse magnetic behaviour of the material. The Wyckoff position also provides insights into the magnetic interactions between neighbouring magnetic atoms. The relative positions and environment of magnetic atoms within the lattice influence the strength and type of magnetic exchange interactions (ferromagnetic, antiferromagnetic, etc.). The Wyckoff position provides insights into the arrangement of ions within the V_6O_{13} lattice. This information helps optimize the crystal structure for efficient lithium-ion diffusion.

6.4 K-Vector of Magnetic Space Group

The k-vector, also known as the propagation vector, defines the spatial periodicity of the magnetic structure within a magnetic space group. It indicates how the magnetic ordering translates and repeats throughout the crystal lattice. By analysing k-vectors, we can find the specific type of magnetic ordering (ferromagnetic, antiferromagnetic, etc.). Table 6.2 represents types of vector for the magnetic space group Pc.

Table 6.2 Types of K-Vector for Pc Magnetic Space Group

k-vector type	coordinates of the vectors of the star	magnetic little co-group	k-vector type of the unitary subgroup	coordinates of the vectors of the star in the unitary subgroup	unitary little co-group
F	(u,0,w)	*m*	F	(u,0,w)	*m*
G	(u,1/2,w)	*m*	G	(u,1/2,w)	*m*
GP	(u,v,w),(u,-v,w)	1	GP	(u,v,w),(u,-v,w)	1

Different magnetic space groups are characterized by specific sets of k-vectors. These vectors can be categorized into various types, each indicating a distinct pattern of magnetic ordering. Some common types include:

- F: Ferromagnetic ordering, where all magnetic moments align in the same direction.
- G: Antiferromagnetic ordering, where magnetic moments align in opposite directions.
- GP: a mixed magnetic ordering that combines characteristics of both ferromagnetism and anti-ferromagnetism.

Table 6.3 Significance of Magnetic Point Group [20]

S.No	Magnetic Point Group	Significance
1.	1	Number of elements of the group (order): 1 This group is not centrosymmetric This group is polar This group is compatible with ferromagnetism
2.	m	Number of elements of the group (order): 2 This group is not centrosymmetric This group is polar This group is compatible with ferromagnetism

V_6O_{13} has magnetic point groups 1 & m are compatible with both ferromagnetism and ferroelectricity.

6.5 Visualization of Magnetic Structures

The MVISUALIZE [21] program enables the visualization of magnetic structures provided in the mcif file format using Jmol software. Jmol visualization of V_6O_{13}'s magnetic structure revelled a complex interplay of magnetic moments within the crystal lattice. The visualizations depict that the vanadium ions carry a magnetic moment due to unpaired electrons in their d orbitals. These magnetic moments exhibit a fascinating arrangement as shown in Figure 6.1, showcasing a combination of ferromagnetic and antiferromagnetic interactions. The intricate arrangement of magnetic moments within the V_6O_{13} crystal lattice contributes to its enhanced lithium-ion diffusion leads to improve battery performance.

Specifically, the combination of ferromagnetic and antiferromagnetic interactions in V_6O_{13} creates a favourable electronic environment for lithium-ion intercalation process which enhances the battery's capacity and rate capability.

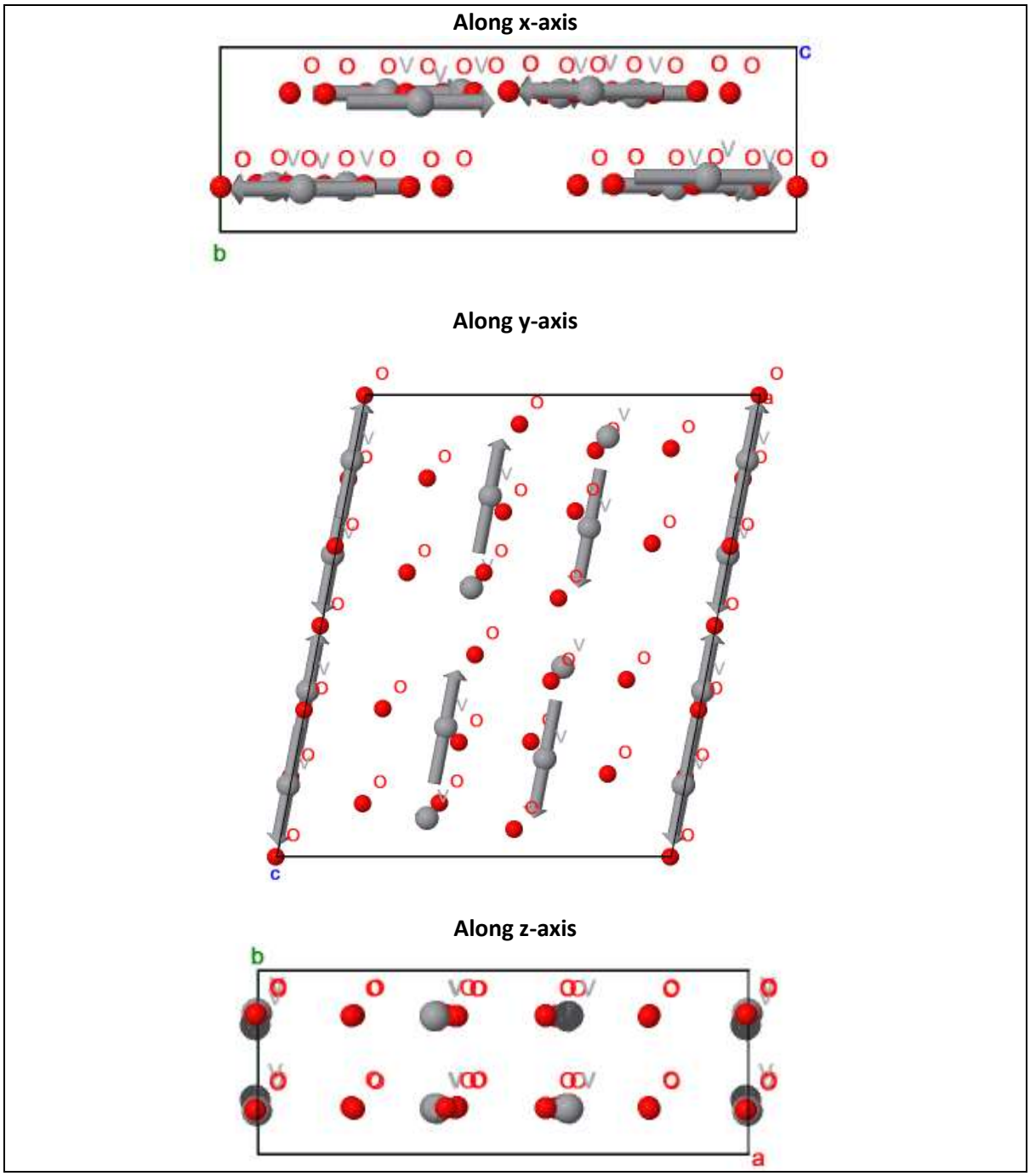

Figure 6.1 Magnetic structure of V_6O_{13}

Conclusion

Our research has established that V_6O_{13} exhibits promising characteristics as a cathode material for future batteries. Its high theoretical capacity, good cycling stability, and environmental friendliness make it a compelling choice for energy storage applications. Additionally, V_6O_{13} has demonstrated potential in other areas, such as catalysis and solar cell technology.

V_6O_{13}, a layered material with promising electrochemical properties, exhibits a unique crystal structure characterized by its point group Cs(m) and space group Pc at low temperature. Our study provides complete insights into the shape, vibrational behaviour, and morphic effect of V_6O_{13}. Furthermore, the Wyckoff position of V_6O_{13} is determined to be 2a. By using the strain determination method, we Calculated the lattice distortion between V_2O_5 and V_6O_{13}, which result to be 1.72156. This degree of lattice distortion is indication of the material's elastic properties.

The 3D visualization of V_6O_{13} reveals a complex and distorted crystal lattice, with vanadium atoms arranged in a distorted octahedral coordination environment. This distortion has a significant impact on the physical properties of V_6O_{13}, such as its electrical conductivity and optical properties.

V_6O_{13} also exhibits a morphic effect, where its crystal structure can be reversibly altered by applying an electric field. This effect is caused by the transformation of the point group from Cs to C1 which primarily affecting the a, b, and c lattice parameters on applying an electric field. The morphic effect has the potential to tune the material properties, such as electrical conductivity and optical properties, for various applications.

The magnetic space group for vanadium oxide (V_6O_{13}) is calculated to Pc (7.24) and its magnetic point group are 1 & m. These designations describe the symmetry of the arrangement of magnetic moments within the crystal lattice of V_6O_{13}. The visualizations of magnetic structure show that the vanadium ions carry a magnetic moment due to unpaired electrons in their d orbitals. V_6O_{13} exhibits a combination of ferromagnetic and antiferromagnetic interactions. This intricate arrangement leads to a net magnetization, but not a complete alignment of all magnetic moments. The combination of ferromagnetic and antiferromagnetic interactions in V_6O_{13} creates a favourable electronic environment for lithium-ion intercalation process which enhances the battery's capacity and rate capability, which can lead to faster charging and discharging rates in batteries.

Future Direction

Vanadium oxide (V_6O_{13}) is a remarkable material with a promising future in various fields, particularly in energy storage. Its high theoretical capacity, excellent cycling stability, and environmental friendliness make it a compelling choice for cathode materials in next-generation batteries. Additionally, V_6O_{13}'s unique magnetic properties can enhance lithium-ion diffusion within the cathode material, leading to faster charging and discharging rates, and improved energy density. Beyond batteries, V_6O_{13} holds promise in catalysis, solar cell technology, and other applications. Its potential as a selective oxidation catalyst, photo catalyst, and transparent conducting electrode opens up exciting avenues for research and development. With further exploration of its morphic effect, tailoring of its magnetic structure, and computational studies, V_6O_{13} is poised to revolutionize various industries and shape the future of energy storage and beyond.

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